Analysis of Mercury Speciation Profiles Currently Used for Atmospheric Chemistry Modeling

By

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Data obtained by the United States Environmental Protection Agency (USEPA) as part of an Information Collection Request (ICR) addressing Section 112 of the Clean Air Act, have been used to estimate speciation for every coal-fired utility boiler in the United States based on type of coal used, type of boiler, and type of controls. Paul Chu and Leonard Levin of EPRI gave a presentation to the Utility Work Group in Washington D.C. on December 18, 2001. The presentation, "EPRI ICR Data Analyses", discusses the methods used to estimate mercury emissions and speciation for coal-fired boilers based on the data collected. It also discusses the limitations: many variables are not directly correlated (LOI, flue gas temperature, flue gas residence time, metal concentrations in coal, effect of SCR, SNCR, NH3), the analyses of coal defines mercury entering boiler, and the analyses assumed that there is no mercury in bottom ash. Despite the room for improvement, speciation for coal-fired boilers is in much better shape than any other category. This is good news if you are myopically interested in coal-fired boilers, but not good news if you are interested in the bigger picture of atmospheric mercury cycling in Wisconsin's environment. Speciation largely determines the distance that mercury emitted from a source is transported [Hg(II) typically is removed from the atmosphere within 100km of the source] and its reactivity. Therefore, inaccurate speciation profiles can result in under or over estimating the contribution to local deposition of a particular source category.

To begin understanding the profiles that are commonly being used today, I will compare two inventories. The first is described in EPRI's final report, "Assessment of Mercury Emissions, Transport, Fate and Cycling for the Continental United States." This is the report often sited when making the argument that over 50% of mercury deposition is attributable to background emissions and not local sources. The second inventory is the Draft 1999 National Emissions Inventory (NEI) currently being developed by USEPA. I will not compare speciation profiles for coal-fired boilers as those profiles are discussed at length elsewhere.

All speciation profiles are shown as three numbers representing the percentages associated with elemental mercury, ionic mercury and particulate mercury respectively (elemental/ionic/particulate).

Mercury Emission Source	EPRI Speciation Profile	EPRI Profile Source	USEPA Speciation Profile	USEPA Profile Source
Municipal Waste Combustors	24 / 75 / 1	Dvonch et al. 1999	22 / 58 / 20	Florida Inventory
Medical Waste Incinerators	4 / 95 / 1	Dvonch et al. 1999	5 / 75 / 20	Florida Inventory
Iron Ore Roasting	85 / 10 / 5	SAI 1998	80 / 10 / 10	RTC 1997 (Other Pt. Source Default)
Residential, Commercial & Ind. Coal Combustion	54 / 44 / 2 B 56 / 42 / 2 A 75 / 24 / 1 L	ICR Averages for bituminous, anthracite & lignite.	50 / 30 / 20	RTC 1997 (Utility/Comm/Res Boilers & Paper Plant Default)
Residential, Commercial & Ind. Oil Combustion	56 / 42 / 2	ICR Averages for anthracite coal	50 / 30 / 20	RTC 1997 (Utility/Comm/Res Boilers & Paper Plant Default)
Commercial & On-Site Incinerators	33 / 50 / 17	RTC 1997 (Medical Waste Incin. w/ 94% control.)	22 / 58 / 20	Same as MWCs
Petroleum Refining	50 / 30 / 20	RTC 1997 (Utility/Comm/Res Boilers & Paper Plant Default)	80 / 10 / 10	RTC 1997 (Other Pt. Source Default)
Coke Ovens	50 / 30 / 20	RTC 1997 (Utility/Comm/Res Boilers & Paper Plant Default)	80 / 10 / 10	RTC 1997 (Other Pt. Source Default)
Oil Burning Electric Utilities	56 / 42 / 2	ICR Averages for anthracite coal	50 / 30 / 20	RTC 1997 (Utility/Comm/Res Boilers & Paper Default)
Wood Burning Utilities	50 / 30 / 20	RTC 1997 (Utility/Comm/Res Boilers & Paper Plant Default)	50 / 30 / 20	RTC 1997 (Utility/Comm/Res Boilers & Paper Plant Default)
Cement Kiln / Portland Cement Manufacturing	74 / 25 / 1	Dvonch et al. 1999	75 / 13 / 12	Florida Inventory
Mines	100 / 0 / 0	Unknown	NA	
Chloralkali / Chlorine Prod.	100 / 0 / 0	Unknown	97 / 3 / 0	Augusta Georgia Data
Lime	50 / 30 / 20	RTC 1997 (Utility/Comm/Res Boilers & Paper Plant Default)	80 / 10 / 10	RTC 1997 (Other Pt. Source Default)
Sewage Sludge Incineration	50 / 30 / 20	RTC 1997 (Utility/Comm/Res Boilers & Paper Plant Default)	22 / 58 / 20	Same as MWCs
Pulp & Paper Plants	50 / 30 / 20	RTC 1997 (Utility/Comm/Res Boilers & Paper Plant Default)	50 / 30 / 20	RTC 1997 (Utility/Comm/Res Boilers & Paper Plant Default)
Lamp Breakage	50 / 30 / 20	RTC 1997 (Utility/Comm/Res Boilers & Paper Plant Default)	NA	
Geothermal Power Plants	50 / 30 / 20	RTC 1997 (Utility/Comm/Res Boilers & Paper Plant Default)	NA	
Engine / Rocket Testing	NA		50 / 30 / 20	RTC 1997 (Utility/Comm/Res Boilers & Paper Plant Default)
Human Cremation	NA		50 / 30 / 20	RTC 1997 (Utility/Comm/Res Boilers & Paper Plant Default)
Hazardous Waste Incin	NA		58 / 20 / 22	RTC 1997
Off-Highway Mobile	NA		90 / 10 / 0	OTAQ email

Reliability of the source is one consideration when comparing speciation profiles. Are the profiles applied to appropriate categories? What is the source of the profile? Let's explore…

Three of the categories in EPRI's study; municipal waste combustors, medical waste incinerators, and cement kilns, reference an article by Dvonch et al. published in *Environmental Science Technology* in 1999. The study, "Use of Elemental Tracers to Source Apportion Mercury in South Florida Precipitation", was not conducted to develop speciation profiles. Sampling performed as part of the 1995 South Florida Atmospheric Mercury Monitoring Study (SoFAMMS) included four municipal waste incinerators, four medical waste incinerators and two cement kilns. All sites were located within a two-county area and no evaluation was done as to how these facilities compare to national averages. Moreover, in 1995, when the samples were taken, there was little confidence in the analytic methods for mercury speciation of exit gases. The study mentions only the percentage of total mercury emitted that was thought to be Hg(II) and these percentages are described as approximate and rough. In applying these percentages of Hg(II) to the source categories, the EPRI study assumed that all but 1% of the remaining Hg was emitted in the elemental form. There is no discussion in the paper to support this assumption. In my opinion, these profiles have low reliability: they are based on dubious speciation methods (and only one of three species to boot) of a few data samples in a specific region of the country.

EPRI's speciation profile for Iron Ore Roasting references a report written by SAI in 1998: "*Modeling Cumulative Outdoor Concentrations of Hazardous Air Pollutants, Volume II: Attachments SYSAPP-98-96/33r1.*" However, the speciation profiles in that report are from an 1996 EPA report: "*Mercury Study. Report to Congress. Volume III: An Assessment of Exposure from Anthropogenic Mercury Emissions in the United States."* Wow! The Report to Congress (RTC)! What is not mentioned in the bibliography is that the 1996 report was a DRAFT. No mention of speciation for non-ferrous metal smelting is made in the final report which was dated 1997.

Many of the speciation profiles have origins in the 1997 (final) USEPA document: "Mercury Study Report to Congress, Volume III: Fate and Transport of Mercury in the Environment EPA-452/R-97-005." This document is so important it is often referred to only as the Report. The Report does provide speciation profiles for 12 categories including "Other Point Sources" and "Area Sources." But the text does not lend confidence to those who need to apply them: "There remains considerable uncertainty as to the actual speciation factors for each point source type" and "Speciated data derived from actual monitoring of sources are a critical research need." Mercury modeling using RELMAP showed that model results are "strongly dependent on the assumed emission speciations." Both the EPRI and USEPA inventories use the Report default for area sources. Both also use the profile 50/30/20 for all point sources not otherwise defined. This profile is for electric utility boilers, commercial and industrial boilers, residential boilers and pulp and paper plants. There is no explanation why the default for "Other Point Sources" (80 / 10 / 10) is not used instead. Additionally, there are several categories in the EPRI study that also use the 50/30/20 profile that may be more appropriately categorized by other profiles: petroleum refining, lime manufacturing,

sewage sludge incineration, lamp breakage, and geothermal power plants, engine/rocket testing, and human cremation.

There are several categories for which USEPA departed from the Report: chlorine production and alkalies cement manufacturing, municipal waste combustors, medical waste incinerators, and off-highway vehicles. Information from Dwight Atkinson, USEPA, indicates that the profile used for chlorine production and alkalies (97/3/0) comes from a presentation of data from the Augusta Georgia chlor-alkali emissions study in September 2000. Matt Landis presented findings of non-elemental mercury concentrations inside the cell room (not captured by other instruments.) Matt estimated that 3-5% of the mercury vapor in the cell room was in non-elemental form. The report cautions: "one should note that this was a limited amount of sampling (ten 2-minute samples, at just one factory, in other words there is some uncertainty around this.) When asked to share the data with other companies (who have interest in changing EPA's original estimate of 30% of mercury being emitted in the divalent form), Matt and his colleagues are described as being "loath to present to this audience" in part because they are "leery of unforeseen policy ramifications." Their caution appears warranted. A few weeks later, Iliam Rosario, an engineer at the Office of Air Quality Planning and Standards, recommended going ahead with the 3-5% divalent mercury speciation. The lower number (3%) is what made it to the final profile. The difference between 30% divalent to 3% divalent may have a significant effect on simulated local deposition. I recommend follow up with a sensitivity simulation using the atmospheric chemistry model.

Three other sources: medical waste incineration, cement manufacture, and municipal waste combustion are based on data collected in the Florida inventory. The distribution of overall divalent reported in the Florida inventory is based on the percentage split listed in the Report for those categories. Like the Dvonch et al. numbers, profiles derived from a small number of sources in a specific region are inherently uncertain. Additionally, I question the validity of mixing two methods: using the elemental / divalent inventory and then splitting the divalent species using the Report.

The off-highway profiles are from undocumented conversations with the EPA Office of Transportation and Air Quality (OTAQ). Follow up needs to be made with Rich Cook, OTAQ's Ann Arbor office, who was planning to conduct Hg emission tests at some point in the future.

This report needs to be used in conjunction with sensitivity modeling using an atmospheric chemistry model and total mass contribution to the inventory to evaluate the needs for future research into mercury speciation profiles. Until the profiles are improved, it is my opinion that all model results will be suspect.